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Reaction of Br⁻ with WF₆: Competition between Charge Transfer and Association; Influence of Temperature, Pressure, and Vibrational Energy

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The rate coefficient for the reaction of Br⁻ with WF₆ was found to be $(6 \pm 2) \times 10^{-10}$ cm³ s⁻¹, independent of temperature and pressure over the ranges 243 to 433 K and 0.2 to 1.2 Torr. The reaction proceeds by two channels: association to form WF_6Br^- and charge transfer to form WF_6^-. The association fraction was found to depend strongly on temperature and pressure, varying from more than 90% association at low temperatures and high pressures to less than 10% association at high temperatures and low pressures. The reaction as studied here is in the falloff regime of association reactions. A steep temperature dependence is observed in the association fraction at high temperatures. This steep temperature dependence is a consequence of WF_6 having many low frequency vibrational levels. Vibrational energy is here found to promote charge transfer more efficiently than does kinetic energy.

Introduction

Association reactions have received much attention in the ion-molecule literature, both experimentally[1] and theoretically.[2-12] A particularly interesting aspect of association arises when association occurs together with another reactive channel, thus raising the question of whether association will "compete" with the other channel or whether it will result in more overall reactivity. The answer to this question is related to the number of intermediates in the reaction. It is sometimes assumed that the rate constants for the different channels are independent of each other.[13] For this situation to obtain, the participation of two (or more) intermediates would be required. An example is the reaction of $CH_3OH_2^+$ with CH_3OH. In this system, both association and nucleophilic displacement are observed,[11,14-16] and association apparently does not compete with displacement.[11,15] The association channel is postulated to involve a proton-bound dimer intermediate which is distinct from the intermediate for nucleophilic displacement.[14-16] In other systems, competition between channels is seen. A particularly good example of this is the reaction of HC_3N^+ with HC_3N, in which condensation competes with three other channels.[17]

In the reaction of Br⁻ with WF_6, association competes with charge transfer. Although the overall reaction is very efficient, the branching fractions show strong dependences on kinetic energy,[18] pressure, and temperature. Vibrational effects are observed in the temperature dependence of the association fraction, and vibrational energy is found to promote charge transfer more efficiently than does kinetic energy. (We use the term *association fraction* in this paper to refer to the portion of the branching fraction which corresponds to association.) The temperature data permit the exothermicity of the reaction to be addressed,[18] and the pressure dependences reveal the pressure regime of the data and raise the question of radiative association. The present paper extends an earlier report[18] and presents additional data on the reaction of Br⁻ with WF_6, examining these data with respect to the above concerns.

Experimental Section

The experiments were performed on a variable-temperature-selected ion flow tube. This experiment has been described previously,[18] and only details pertinent to the present experiment will be discussed. The temperature was raised by the use of resistance heaters and lowered by passing methanol cooled in an external refrigerator through heat exchange coils. Below room temperature, the temperature was stable within two degrees, as monitored by six platinum resistance thermometers placed along the length of the flow tube. Much wider temperature variations occurred for the data taken above room temperature (± 10 K at 433 K). The low temperature limit (243 K) was determined by the freezing of WF_6 in the inlet lines.

Br⁻ was made from CF_3Br in a high pressure electron impact ion source. The flow of WF_6 (measured and controlled by an MKS mass flow controller) was found to vary depending upon the length of time the gas had remained in the stainless steel sampling volume used in the reaction inlet system. It was necessary to condition the inlet system and to use the WF_6 within a few hours after filling the sampling volume. This problem is discussed in more detail elsewhere.[18] This problem limited the accuracy with which rate coefficients could be measured to $\pm 35\%$. The precision is $\pm 25\%$. No product was observed that could be attributed to impurities. The only observable effect of the WF_6 inlet problem was that the measured rate constants were smaller after the inlet had been filled for several hours.

The reproducibility of the branching fraction measurements was a few percent, an indication that the inlet system problem did not affect these measurements. The primary ion is mass 80 Dalton (Br⁻), and the product ions are masses 298 Dalton (WF_6^-) and 378 Dalton (WF_6Br^-). (The masses are given as averages since the experiments were done with low mass resolution, in order to minimize mass discrimination. All isotopes were detected as one peak and the width of the peaks was such that all isotopes should have been detected.) The branching fractions are affected by mass discrimination only between 298 and 378 Dalton, and this effect is expected to be small. Mass discrimination between 80 and 298 Dalton or 378 Dalton may be significant, but product ion increase balanced reactant ion loss to within 30%, indicating

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TABLE I: Percentage Association Expressed as $A + B\{M\}$ (Reaction 1)

temp (K)	A (%)	B (%) (Torr^{-1})	correlation coefficient
243	86	7	0.96
261	73	18	0.95
296	55	22	0.82
353	30	11	0.99
433	6	7	0.85

that mass discrimination was not a severe problem. The reasonable agreement may be due to the opposing effects of mass discrimination in the quadrupole and differing diffusive losses in the flow tube. The absolute branching fractions are thought to be accurate to within 30%. Nevertheless, we could not quantify the mass discrimination, and we have not attempted to correct the data for this effect. The accuracy is therefore quoted conservatively as 30%. Differences between the present data and data taken at the University of Birmingham[18] are on the order of 10%. As indicated above, the relative accuracy (as determined by the precision) is much better, being on the order of a few percent.

Results

The total rate constant for the reaction

$$Br^- + WF_6 \rightarrow WF_6Br^- \tag{1a}$$

$$\rightarrow WF_6^- + Br \tag{1b}$$

was found to be $(6 \pm 2) \times 10^{-10}$ cm^3 s^{-1}, independent of pressure and temperature (within experimental precision) over the entire range of experimental conditions used in this study. The rate constants for this and several other ion reactions with WF_6 varied approximately as the appropriate reduced mass ratio, as they must do if all are essentially the collisional values or if all of the reactions have the same non-unitary efficiency.[18] The latter is improbable, and we conclude that the measured values are equal to the collisional value within experimental uncertainty. No collisional value can be calculated, since the polarizability is unknown. A separate measurement of the rate constant at the University of Birmingham resulted in a value in good agreement with the present value, independent of temperature between 300 and 510 K, and independent of energy over the range 0.039 to 1.13 eV.[18]

In contrast to the lack of dependence of the overall rate constant on pressure, temperature, and energy, the product distribution is highly dependent on both temperature and pressure. Figure 1 shows a plot of the association fraction, expressed as a percent, versus pressure for five different temperatures. As the temperature decreases, the percent association increases dramatically. A significant increase in percent association also occurs with increasing pressure. In the most dramatic case (296 K), the percent association increases from 60% at 0.2 Torr to 73% at 0.8 Torr. The Birmingham data are again in good agreement with the present results, the Birmingham point at 300 K and 0.5 Torr being 72% compared to 66% percent for the present value (296 K). As indicated in Figure 1, the percent association was found to be linearly dependent on pressure in the pressure range accessible in our experiment. Table I shows the results of least squares fits for the percent association to the form $A + B\{M\}$, where A and B are constants and $\{M\}$ is the gas pressure. These fits are shown graphically in Figure 1 as solid lines. The correlation coefficients are also listed in Table I and range from 0.99 to 0.82. The intercepts in these fits are found to be nonzero. The linearity is probably a consequence of the limited pressure range of the data, as discussed below.

Discussion

The fact that the overall rate constant is independent of temperature and pressure, while the branching fractions change with either temperature or pressure, is a clear indication that association and charge transfer compete with each other in a direct sense. This competition reinforces the need for caution when analyzing data such as these in terms of separable bimolecular and termolecular components. Some cases in the literature show asso-
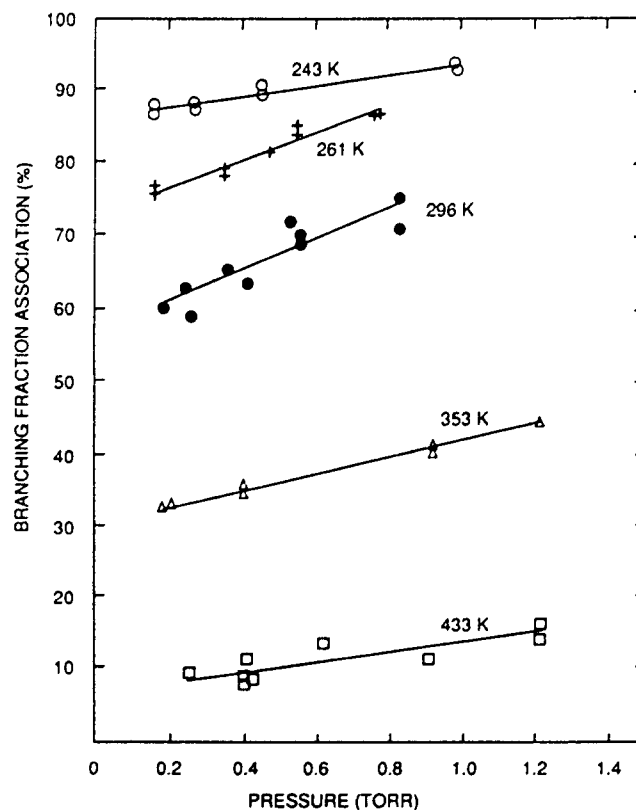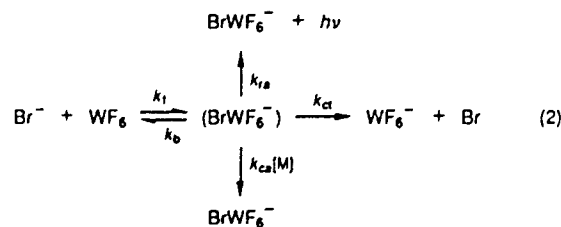

Figure 1. Percent of WF_6Br^- product as a function of pressure at five temperatures. Open circles, plusses, closed circles, triangles, and squares represent temperatures of 243, 261, 296, 353, and 433 K, respectively.

ciation preempting other reaction, as in the present case (see also Sen et al.[17]), and, in contrast, other cases in which association adds to the total reactivity while the rate constant for the other channel remains constant (see for example Morris et al.[15]). Competition between the two channels, association and charge transfer, is an indication that they may proceed through a common intermediate. In at least one case where the two channels do not compete, two intermediates are thought to be involved.[15] A reaction such as that between Br^- and WF_6 may be expected to have a single deep well and therefore a single intermediate. As an indication of this possibility for similar reacting species, the strength of the bond between F^- and WF_6 is 3 eV.[19] The Br^--WF_6 bond strength is unknown.

The simplest mechanism for the reaction between Br^- and WF_6 studied here is shown in eq 2, where k_f, k_b, k_{ct}, k_{ra}, and k_{ca} are

$$BrWF_6^- + h\nu$$

$$\uparrow k_{ra}$$

$$Br^- + WF_6 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (BrWF_6^-) \xrightarrow{k_{ct}} WF_6^- + Br \tag{2}$$

$$\downarrow k_{ca}\{M\}$$

$$BrWF_6^-$$

the rate coefficients for complex formation, complex dissociation into reactants, charge transfer, radiative association, and collisional association, respectively. $\{M\}$ is the density of the helium buffer gas. This mechanism assumes that the reaction proceeds through a single intermediate. The fact that the rate constant for the reaction is approximately equal to the collision rate constant indicates that $k_b \ll k_{ct} + k_{ra} + k_{ca}\{M\}$, but a small amount of dissociation into reactants cannot be excluded.

At least two possible mechanisms may be suggested to explain the fact that the measured branching fractions have non-zero intercepts at zero pressure. One possibility is that the reaction

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may involve both radiative and collisional stabilization and that the experimental conditions may correspond to the low pressure regime of three-body reactions. In this case the intercept of the branching fraction plot would be the rate constant for radiative association. Alternatively, the reaction may be in the falloff regime. This is the pressure range in which dissociation of the intermediate complex competes with stabilization of the complex. For this reaction, dissociation would include dissociation back into the reactants as well as dissociation into the charge-transfer products. As explained previously, k_b is small, and charge transfer is the dominant contribution to the dissociation channel, at least over much of the range of experimental conditions. Mathematically, a reaction of the present type is in the falloff regime when $k_b + k_{ct} \approx k_{ra} + k_{ca}[M]$. The competition between charge transfer and association suggests that the charge-transfer reaction is approximately thermoneutral.[18] A careful look at the data shows that the reaction must be in the falloff regime under the present conditions. Efficiencies for the association channel range from a few percent to over 90%. The criterion for the reaction being in the low pressure regime is that the stabilization rate in the low pressure regime is much less than the dissociation rate, and this criterion is not satisfied. This failure is especially evident at low temperatures. At room temperature and below, the stabilization rate exceeds the dissociation (i.e. charge transfer) rate, since the association channel accounts for over 50% of the reactivity. At the lowest temperature (243 K) and highest pressures, the reaction must be close to the high pressure limit, since the efficiency for association is approaching 100% (i.e. the association fraction is approaching 100%). The transition from intermediate to high pressure kinetics is evident in the slopes of the plots of percent association versus pressure. Above room temperature, the slopes increase with decreasing temperature (increasing efficiency for association) as expected for reactions in the low pressure regime. However, below room temperature the slopes decrease, indicating that the high pressure limit is approached. In the high pressure limit the slopes would be zero. Since the data must be in the falloff regime, the linearity of the data results simply from the limited pressure range of the experiments.

The question arises whether any radiative association is occurring in the reaction of Br⁻ with WF₆. In a number of similar systems involving halide ions bonding to a halogenated neutral species, radiative association has been suggested to occur.[20,21] Evidence for this was the observation of nonzero intercepts that were independent of the identity of the buffer gas in plots of second-order rate constant versus pressure. Recent work at low pressure in an ion cyclotron resonance (ICR) apparatus (where any association must be radiative) has shown that in two of these systems, i.e., F⁻ and Cl⁻ plus BF₃, no association was observed.[22] The production of BF₄⁻ and BF₃Cl⁻ was instead found to be due to impurities in the BF₃. Thus radiative association is not important in at least some of these systems. A similar test in an ICR apparatus would show whether radiative association occurs in the reaction of Br⁻ with WF₆. Unfortunately, WF₆ is difficult to work with due to its reactive nature, as discussed in the Experimental Section, and the test has not yet been performed. The problem is even more severe at low pressures, making the measurements in an ion cyclotron resonance apparatus especially difficult. Some work on the reaction of F⁻ with WF₆ has been performed using an ICR and does suggest the occurrence of association at low pressure.[19] In that ICR study, however, the rate constants differed by over an order of magnitude from those obtained in the SIFT experiments.[18] This disparity again reflects the difficulty in working with WF₆, particularly under the low pressure conditions of the ICR. In light of the above considerations, it remains an open question whether any radiative association is occurring in the Br⁻ plus WF₆ and F⁻ plus WF₆ systems.

Another interesting aspect of the data is the steep temperature dependence of the branching ratio that is found at high tem-
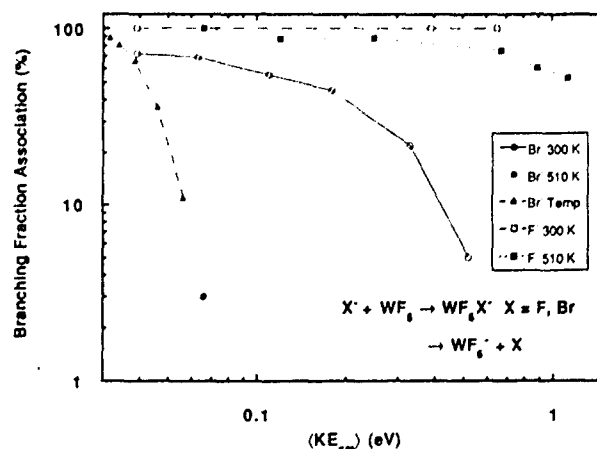

Figure 2. Percent of WF₆Br⁻ and WF₇⁻ product as a function of average center of mass kinetic energy ($\langle KE_{cm} \rangle$). The data all correspond to a number density of 3.62×10^{16} cm⁻³, except for the 510 K data which correspond to a number density of 9.5×10^{15} cm⁻³. Open and closed circles represent the $\langle KE_{cm} \rangle$ data for the Br⁻ reaction with WF₆ at 300 and 510 K.[18] Closed triangles represent the data for this reaction taken as a function of temperature converted to $\langle KE_{cm} \rangle$ by $\langle KE_{cm} \rangle = 3/2kT$. Open and closed squares represent the $\langle KE_{cm} \rangle$ data for the F⁻ reaction with WF₆ at 300 and 510 K.[18]

peratures. An approximate upper limit to the temperature dependence can be obtained by using low pressure association theory. The rate constants for many ion–molecule association reactions have temperature dependences on the order of $T^{-r/2}$, where r is the total number of rotational degrees of freedom in the reactants.[2,3,5-8] At high temperature, the dependence observed in the present work is much steeper than is given by this expression. The $T^{-r/2}$ dependence comes from the dependence of the rate constant on the rotational partition function alone. When the vibrational partition function is taken into account, much steeper dependences are found.[9] Theory which includes vibrational effects[9] gives the temperature dependence as $T^{-r/2}\Pi_i\{1 - \exp(-h\nu_i/kT)\}$, where the ν_i are the vibrational frequencies of the reactants. This formula yields temperature dependences of $T^{-7.9}$ and $T^{-8.5}$ over the temperature ranges of 350 to 400 K and 400 to 450 K, respectively. These dependences are stronger than those found in the present study and are a consequence of the fact that WF₆ has a large number of low frequency vibrational levels.[23] The fact that the calculated temperature dependences are greater than the experimental values is further evidence that the measurements are not in the low pressure limit. The low pressure theory does, however, indicate that the steep temperature dependence observed in this study is reasonable.

The importance of the low frequency vibrations of WF₆ in this reaction is observed in another aspect of the data. We have previously reported the association fraction for this reaction as a function of average center of mass kinetic energy at 300 and 510 K. These measurements were made in the University of Birmingham variable-temperature-selected ion flow drift tube.[18] Since the time that these data were published, we have developed a technique to derive the dependence of rate constants or branching fractions on the internal temperature of the reactant neutral (for monatomic ions).[24-30] The technique involves comparing rate

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constants or branching fractions at a particular average kinetic energy but at different temperatures. If the ion is monatomic, as in the present case, any difference may then be attributed to the internal temperature of the neutral. In reaction 1, the overall rate constant is independent of temperature; so there is no dependence of the rate constant on internal temperature. The branching fraction, however, shows a large dependence on the internal temperature of WF_6. This is best seen in Figure 2. Several sets of data are plotted: (1) the kinetic energy dependence measured in the Birmingham apparatus at 300 K[18] (open circles); (2) the kinetic energy dependence measured in the Birmingham apparatus at 510 K[18] (closed circles); (3) the temperature dependence of the present data (closed triangles) where temperature has been converted to average center of mass kinetic energy ($\langle KE_{cm}\rangle$) by $\langle KE_{cm}\rangle = 3/2kT$. Also plotted are the Birmingham data[18] for the reaction of F^- with WF_6 at 300 K (open squares) and 510 K (closed squares), since they show a similar effect. The data all correspond to a number density of 3.6×10^{16} cm^{-3}, except for the data at 510 K, which correspond to a number density of 9.5×10^{15} cm^{-3} (no data were taken at any other number density).

The effect of WF_6 vibrations (and rotations) is seen by comparing data at a particular $\langle KE_{cm}\rangle$ but at different temperatures. Figure 2 shows large differences between the influence of temperature and kinetic energy. At a $\langle KE_{cm}\rangle$ of 0.046 eV, the branching fraction decreases from 70% to 36% as the temperature changes from 300 to 353 K, a rather large change for a small temperature difference. Even more pronounced are the effects shown in the data at 0.066 eV, where the association fraction at 300 K is 67% while that at 510 K is only 3%. A 70% increase in temperature caused the association fraction to decrease by a factor of 22. These large effects are attributed to the internal temperature of the WF_6 neutral. Rotational effects are usually much smaller than those observed here,[24-32] and the observed dependence is in all likelihood due largely to the low frequency vibrations of WF_6.

The observations made here raise an important question: do translational and vibrational energy have the same effect on the branching fraction? At 510 K and with no additional kinetic energy from the drift field, the total energy (vibrational, rotational, and translational) available is 0.6 eV. This quantity is obtained by calculating the average vibrational energy based on the vibrational frequencies of Gaunt[23] and assuming no anharmonicity. At 300 K, the total average internal energy is 0.17 eV (vibrations and rotations). The $\langle KE_{cm}\rangle$ at 300 K corresponding to 0.6 eV total energy is then 0.43 eV. The corresponding association fractions at a total energy of 0.6 eV are 10% and 3% at 300 and 510 K, respectively. The conclusion is that internal energy is more

efficient at driving the charge-transfer reaction (or alternatively retarding the association reaction) than is kinetic energy. As stated previously, the difference in efficiency is probably due largely to vibrational energy rather than to rotational energy.

Similar conclusions can be drawn from the data on the reaction of F^- with WF_6.[18] The reaction proceeds by the same two channels, association and charge transfer. At 300 K, only association is observed at all $\langle KE_{cm}\rangle$ studied. Association was also the only channel observed at 510 K with no added kinetic energy from the drift field. At the higher temperature, added kinetic energy reduces the efficiency of the association channel to below 100%. At the highest $\langle KE_{cm}\rangle$ studied (1.13 eV) the efficiency is 53%. Total energy cannot explain the difference. Just as in the reaction of Br^- with WF_6, vibrational excitation is more efficient at promoting the charge transfer than is translational energy.

Conclusions

Rate constants and branching fractions for Br^- reacting with WF_6 have been measured. The pathways are association, forming WF_6Br^-, and charge transfer, forming WF_6^-. While the rate constant for loss of reactant ion was found to be independent of temperature and pressure and corresponds to an overall reaction efficiency close to 100%, the branching fraction was found to be strongly dependent on both temperature and pressure. The fact that the overall reaction proceeds with nearly unit efficiency while the branching fraction changes indicates that the two channels compete with each other, i.e., one channel increases only at the expense of the other. This competition may indicate that the reaction proceeds through a common intermediate.

The data in this work pertain to the falloff regime of association reactions, as evident from the fact that the efficiencies for association vary from less than 10% to more than 90% over the range of conditions studied. The slopes of the branching fractions in Figure 1 have a maximum in the middle of the temperature range studied here. This further indicates falloff behavior. No conclusions can be made on whether radiative association is occurring.

The temperature dependence of the branching fraction is large at the highest temperature studied (lowest fraction association). The large temperature dependence appears to be a consequence of WF_6 having many low frequency vibrational levels. The importance of the numerous low frequency vibrations is observable in another way: when the present results are combined with previously published data on the kinetic energy dependence of this reaction, it can be shown that vibrational energy is more efficient at promoting the charge-transfer channel than is translational energy. A similar effect is seen in the reaction of F^- with WF_6.

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